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Mn(III)-tetraarylporphyrins bearing covalently bonded crown-ethers: synthesis and catalytic activity in 1-dodecene epoxidation promoted by aqueous $HOCl/OCl^-$

Stefano Banfi *, Amedea Manfredi, Fernando Montanari, Gianluca Pozzi, Silvio Quici, Felice Ursino

Centro CNR and Dipartimento di Chimica Organica e Industriale dell'Università, Via Golgi 19, 20133 Milano, Italy

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Abstract

Mn(III)-complexes of tetraarylporphyrins **1–4** bearing a crown-ether covalently linked through a single flexible chain have been synthesized. Their basic frame is that of the robust tetra-(2,6-dichlorophenyl)porphyrin **5** and the chain is connected by ether linkage either to the *ortho* (**1–2**) or to the *meta* positions (**3–4**) of one *meso*-aryl group. Catalytic efficiency was tested in the epoxidation of the poorly reactive 1-dodecene at 0°C under CH_2Cl_2/H_2O two-phase conditions in the presence of NaOCl (pH 9.5–10.0) as oxygen donor. The results obtained led us to propose a general acid/base catalysis as an explanation for the positive effect of crown-ethers in the alkene epoxidations with this catalytic system.

Keywords: Functionalized Mn(III)-porphyrins; Crown ethers; 1-Dodecene epoxidation; NaOCl promoted epoxidation

1. Introduction

Oxidation reactions catalyzed by Mn(III)-tetraarylporphyrins in the presence of aqueous NaOCl under two-phase conditions were first described by Tabushi [1]. Subsequently, Meunier [2] found that the addition of heterocyclic nitrogen bases acting as axial ligand for the metal led to a remarkable increase of reaction rate in alkene epoxidations. Several other research groups used aqueous NaOCl as oxygen donor in hydrocarbon oxygenations, but in any case the presence of quaternary ammonium salts was compulsory in order to ensure the transfer of the primary oxidant (OCl^-) in the organic phase [3]. We showed that a further rate enhancement in NaOCl promoted oxygenations is obtained by lowering the pH of diluted commercial bleach from 12.5 to 9.5–10.0. At this pH, the weak hypochlorous acid thus generated, spontaneously allots between the aqueous phase and the CH_2Cl_2 solution containing the substrate and the Mn-porphyrin [4]a. The effective oxygen donor is now HOCl, hence the presence of a phase transfer catalyst is not strictly necessary [4]b. Nevertheless, using dibenzo-18-crown-6 (DB18-C-6) instead of quaternary ammonium salts at pH 9.5–10.0, a remarkable positive effect was observed in the epoxidation of poorly reactive α-olefins. In fact, at 0°C with

* Corresponding author

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substrate/catalyst (S/P) ratio = 200 and initial catalyst concentration $[P]_0 = 1.25 \times 10^{-3}$ M, 1-dodecene was converted into the corresponding epoxide in a few minutes and 100% selectivity. This effect could not be explained in terms of phase transfer catalysis since DB18-C-6 has a very poor extraction capability for OCl^-, hence its true function remained unclear [5].

In the course of our investigations on the effect of co-catalysts on the rate of Mn-porphyrin catalyzed hydrocarbon oxygenations, we disclosed the beneficial effect of connecting such species to the porphyrin frame through single flexible chains [6]. In the case of heterocyclic nitrogen bases and/or carboxylic acids, the improvement of the catalytic activity of tailed Mn(III)-porphyrins with respect to that of non-functionalized complexes was related to the favourable intramolecular interaction between the metal centre and the co-catalyst.

These results prompted us to verify if a similar effect could be observed when crown-ether functionalized Mn(III)-tetraarylporphyrins were used as catalysts in alkene epoxidations with NaOCl under two-phase conditions.

2. Results and discussion

Bis-macrocyclic systems composed of a porphyrin covalently linked to a polyheteromacrocycle are the starting materials for building biomimetic models of active sites in biological processes and supramolecular structures of interest in material science [7]. Despite the wide interest in biomimetic hydrocarbon oxygenations, macrocycle functionalized porphyrins have never been used as model of monooxygenases. In most of the reported examples the two moieties are linked through two bridges, thus

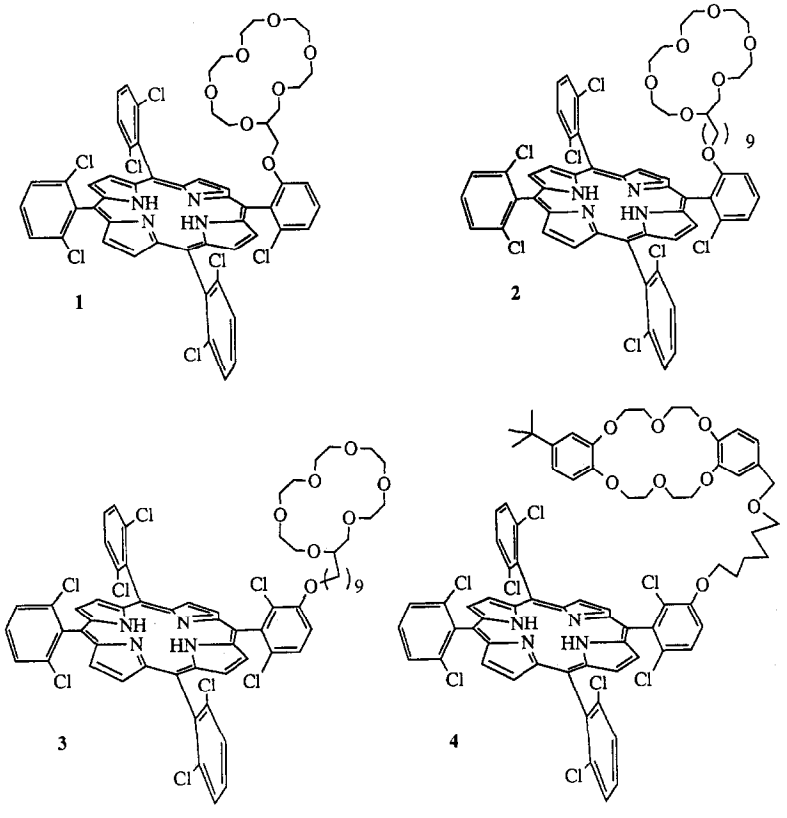


Fig. 1. Structure of new porphyrins **1–4**.

restricting the conformational freedom in order to create a preorganized host cavity [8]. On the contrary, few compounds in which the porphyrin and the polyheteromacrocycle are linked through a single bridge have been described [9].

We have designed porphyrins **1–4** (Fig. 1) belonging to this last class, trusting on our precedent works in which we found that the flexibility of the system does not impair the interaction between the reaction centre and the linked co-catalyst. Moreover, this approach is synthetically easier than the multi-links one and allows to maintain a robust porphyrin structure, i.e., similar to that of the 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin **5**.

The crown-ether must contain a functional group suitable for the linkage to the phenol residue present on porphyrins **6** and **7** and its structure should be as similar as possible to that of DB18-C-6, which gave the best results in alkene epoxidations catalyzed by Mn-**5** [5]. In a first attempt we linked two derivatives of 18-crown-6 (**8–9**) to porphyrins **6** and **7** (Scheme 1), because of their availability through a reported synthetic procedure [10]a. For sake of comparison, 1-alkene epoxidation catalyzed by Mn-**5** in the presence of the lipophilic dicyclohexano-18-crown-6 (DCh18-C-6) were carried out. They gave worse results than those carried out in the presence of DB18-C-6, so we have also prepared the DB18-C-6 functionalized porphyrin **4**.

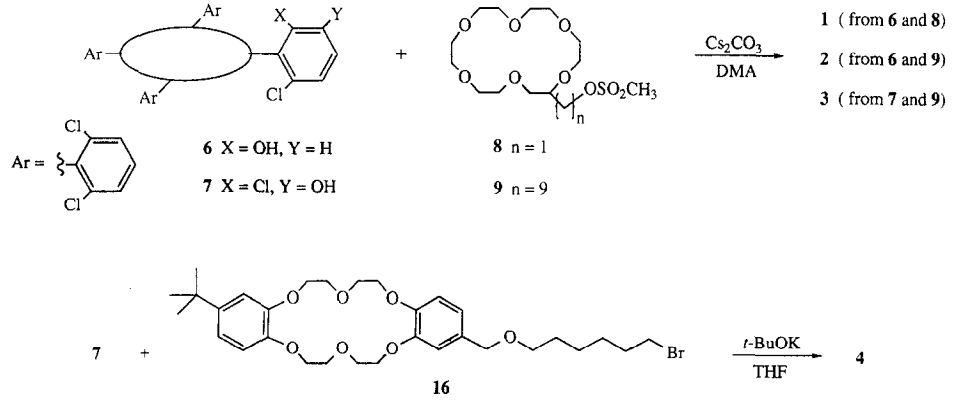
Free-base porphyrins **1–3** were synthesized by reacting at room-temperature hydroxy-functionalized tetraarylporphyrins **6** or **7** with the proper 2-(ω-methanesulphonylalkyl)-18-crown-6 **8** or **9** in dimethylacetamide (DMA) and Cs_2CO_3 as base (Scheme 1).

Porphyrin **6** was synthesized by mixed condensation of 2-chloro-6-methoxybenzaldehyde **10** and 2,6-dichlorobenzaldehyde with pyrrole (molar ratios 1 : 3 : 4), followed by deprotection of the methoxy group with BBr_3. Porphyrin **7** was analogously obtained using 2,6-dichloro-3-methoxybenzaldehyde **11** instead of aldehyde **10** [11].

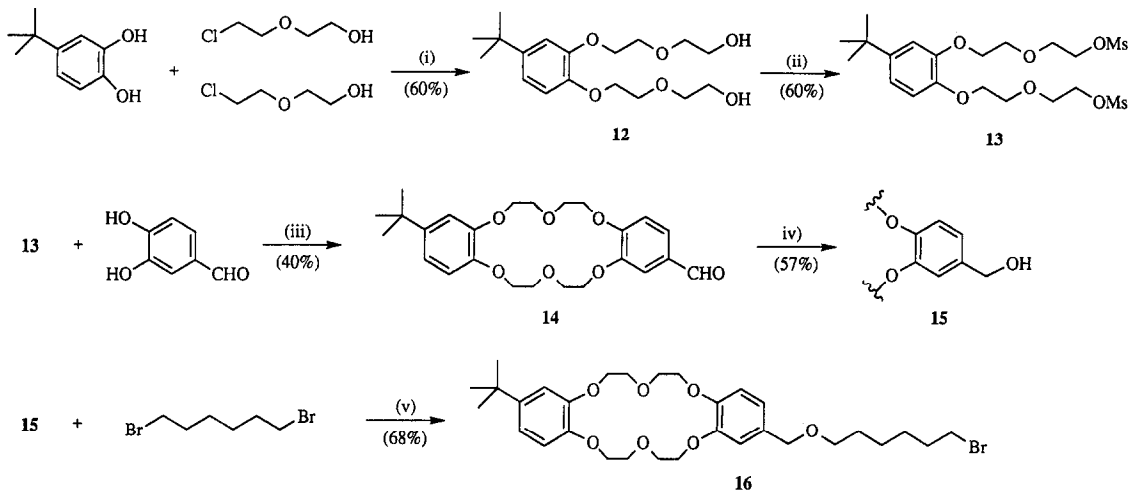
Synthesis of porphyrin **4** required the preparation of the unprecedently reported dibenzo 18-crown-6 derivative **16**, according to Scheme 2. Aldehyde **14** was obtained via standard reactions of dibenzo-crown chemistry [10]b and was then reduced to the corresponding alcohol **15** with $NaBH_4$ in EtOH at room temperature. Alcohol **15** was alkylated with a large excess of 1,6-dibromohexane in the presence of NaH in dry THF, affording the ω-bromo derivative **16**. The final condensation of porphyrin **7** with **16** was carried out in THF and *t*-BuOK as base.

Tetraarylporphyrins **1-4** were quantitatively converted into the corresponding Mn(III) complexes (Mn-**1**-Mn-**4**) by treatment with $Mn(OAc)_2 \cdot 4H_2O$ in refluxing DMF.

The catalytic activity of Mn-**1**-Mn-**4** (P) was tested in 1-dodecene (S) epoxidation in the pres-



Scheme 1. Last step of the synthesis of porphyrins **1–4**.



(i) NaOH, EtOH, reflux; (ii) CH_3SO_2Cl, Py, 0 - 5 °C; (iii) *t*-BuOK, THF, reflux; (iv) $NaBH_4$, $EtOH_{aq}$, RT; (v) NaH, THF, RT.

Scheme 2. Synthetic pathway for functionalised crown-ether **16**.

ence of an excess of aqueous NaOCl 0.7 M whose pH was adjusted at 9.5–10.0 with solid $NaHCO_3$. Reactions were carried out at 0°C with catalyst concentration of 4×10^{-4} M under H_2O/CH_2Cl_2 two-phase conditions. Catalyst concentration was kept three time lower with respect to that of our precedent experiments [5], with the aim to stress the proximity effect of the covalently linked crown-ether. *N*-Hexylimidazole (L) was added as axial ligand to the CH_2Cl_2 solution of catalyst and alkene before starting the reaction. In each case substrate/catalyst (S/P) molar ratio was equal to 500 and L/P ratio was = 1. The progress of the reactions was followed by gas-chromatographic analysis of the organic phase (internal standard method). The catalytic activity of Mn-**1**-Mn-**4** was compared to that of Mn-**5**; with this last catalyst, reactions were run in the presence of either DB18-C-6 or DCh18-C-6 (CE), with CE/Mn-**5** = 1 or 10. Results are reported in Table 1.

Entries 1–4 confirm what we had previously reported about the positive effect of crown-

Table 1
1-Dodecene epoxidation by $HOCl/OCl^-$ catalyzed by Mn-**1**–**5** complexes [a]

Entry	Catalyst(P)	CE	CE/P	Conv. Turnover [b](at 5 min)		Conv. Turnover [b](at 60 min)	
1	Mn-**5**	–	–	27%	135	41%	205
2	Mn-**5**	DB18-C-6	1	21%	105	45%	225
3	Mn-**5**	DB18-C-6	10	41%	205	62%	310
4	Mn-**5**	DCh18-C-6	10	18%	90	50%	250
5	Mn-**1**	–	–	20%	100	44%	220
6	Mn-**2**	–	–	1%	5	17%	85
7	Mn-**3**	–	–	28%	140	54%	270
8	Mn-**4**	–	–	18%	90	30%	150

[a] Reaction conditions: CH_2Cl_2/H_2O $v/v = 1.25/1$; $T = 0°C$; pH 9.5–10.0; 1-dodecene/P = 500; L = *N*-hexylimidazole, L/P = 1; $[P]_0 = 4.0 \times 10^{-4}$ M.
[b] Average values based on three independent experiments.

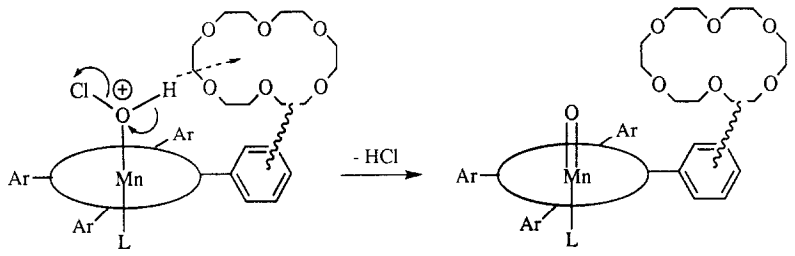


Fig. 2. Suggested mechanism for high valent Mn-oxo species formation through 'pull' effect exerted by the C.E. moiety in catalysts Mn **1** – Mn **4**.

ethers on the catalytic activity of Mn-**5**. The CE/P ratio strongly influences the outcome of the reactions (entries 2 and 3), the best results being obtained with CE/P = 10. We compared the effect of the structure of the crown-ether using DB18-C-6 and DCh18-C-6 as lipophilic models of rigid and flexible polyoxamacrocycles, respectively (entry 3 and 4). DB18-C-6 gave both the highest initial rate (evaluated at 5 min) and overall turnover at 60 min.

Among the bis-macrocylic compounds Mn-**1**-Mn-**4**, Mn-**3** proved to be the best catalyst, its activity approaching that of Mn-**5** with CE/P = 10 (entries 7 and 3, respectively), while Mn-**1** gave results comparable to those obtained with Mn-**5** and DB18-C-6 at CE/P = 1 (entries 5 and 2). Unexpectedly, catalysts Mn-**4** and Mn-**2** were even less active than Mn-**5** used in the absence of phase transfer catalyst.

The following trends emerged from our experiments:

(i) for crown-ether functionalized porphyrins, the effectiveness of rigid and flexible CE is reversed with respect to that found in entries 3 and 4; (ii) catalysts bearing the same CE connected through a C-9 chain in *ortho* (entry 6) or *meta* (entry 7) position of a *meso*-aryl group show a striking different activity; iii) the length of the connecting chain placed in the *ortho*-position strongly affects catalysts performances (entries 5 and 6).

These results are rather puzzling and only a tentative explanation will be proposed.

Effect of CE structure: The crown-ether moiety in Mn-**4** is more sterically demanding with respect to the 18-C-6 present on catalyst Mn-**3**. Since the linkage imposes a degree of proximity between the two macrocycles, we suppose that steric hindrance is the cause of the lower catalytic activity of Mn-**4** with respect to Mn-**3** [1].

Effect of linkage position and of chain length: Catalyst Mn-**2** features seven chlorine atoms and one alkoxyl group in the *ortho*-positions of the *meso*-phenyls while in Mn-**3** the same positions are occupied by eight chlorine atoms. The lack of protection even in only one of the *ortho*-positions decreases the stability of Mn-porphyrins under our reaction conditions [6]. However, the very low catalytic activity of Mn-**2** could be only partially ascribed to this effect. CPK models of Mn-**2** and Mn-**3** show that for the first compound the C-9 chain in the *ortho*-position forces the terminal crown-ether far away from the core of the porphyrin ring. In the case of Mn-**3** the linkage in the *meta*-position allows the approach of the co-catalyst to the metal site. Since the co-catalytic effect of CEs cannot be related to an efficient transfer of OCl^- in the organic phase [5] an alternative explanation for the CE effect should be seek.

In the light of the present results, we assumed that in the organic phase the CE could act on the intermediate HOCl/Mn-porphyrin complex through a 'pull' effect [12]. The basic oxygen

[1] The bulky *t*-butyl group present in the DB18-C-6 derivative linked to the porphyrin ring was introduced as a probe for NMR analysis of compound **4**. It is particularly useful for the ^{1}H-NMR study of molecular recognition properties of **4** derivatives used as ditopic receptors.

atoms might facilitate the cleavage of the O–H bond (Fig. 2) thus making easier the formation of the high valent Mn-oxo species, responsible for the oxygen transfer to the substrate.

The higher catalytic activity of Mn-**1** with respect to Mn-**2** strongly supports this view: indeed, as argued by CPK models, the C-1 chain in the *ortho*-position keeps the CE in the proximity of the Mn atom. In the case of Mn-**1** the lacking of steric protection due to the absence of a chlorine atom is partially offset by the presence of the bulky 18-C-6.

Furthermore, if the previous hypothesis was correct, the addition of a potassium salt to our biphase system would have inhibited the catalytic activity of the Mn-porphyrins. Indeed, the affinity of 18-C-6 derivatives for K^+ is higher than that for Na^+ [13] and the complexation of the CE with K^+, lowering the electronic density at the oxygen sites, should prevent the 'pull' effect to be realized. A second series of experiments (Table 2) confirmed that the outcome of the catalytic epoxidation upon addition of KOAc is actually influenced in this sense.

The effect of KOAc was first investigated in 1-dodecene epoxidations run under the reaction conditions reported in our preceding paper [5]; the high reaction rates thus obtained should emphasize the forecasted negative influence of K^+. Entries 1 and 2 show that the conversion of the olefin halves upon addition of a slight excess of KOAc with respect to the externally added DB-18-C-6. The same effect was observed when the bis-macrocyclic complex Mn-**4** was used as catalyst under the reaction conditions described in this work (entries 3 and 4). In order to confirm that KOAc alone does not hamper the activity of the catalytic system, two more experiments were carried out (entries 5 and 6). We compared the conversion of the substrate in the absence of CE, either in the absence or in the presence of the potassium salt (entries 5 and 6, respectively). Any difference was found, thus showing that the negative influence observed in entries 2 and 4 is only related to the presence of both KOAc and CE.

3. Conclusions

The reported results clearly indicate that the synthetic effort we put into the preparation of crown-ether functionalized tetraarylporphyrins have not been rewarded in terms of catalytic activity. Anyway, the behaviour of complexes Mn-**1**-Mn-**4** in 1-dodecene epoxidation promoted by $HOCl/OCl^-$ allowed us to postulate a general acid-base catalysis as the origin of the co-catalytic effect of crown-ethers, which was not identified in our previous work. Furthermore, porphyrins **1**–**4** are potentially interesting ditopic receptors for the molecular recognition of amino-acids or functionalized ammonium salts as we are currently investigating.

Table 2
1-Dodecene epoxidation by $HOCl/OCl^-$ catalyzed by Mn-**5** and Mn-**4** complexes Effect of KOAc [a]

Entry	Catalyst(P)	$[P]_0$(M)	L/P	CE	CE/P	K^+/P	Conv.	Turnover [b](at 5 min)
1	Mn-**5**	1.25×10^{-3}	1	DB18-C-6	10	–	85%	425
2	Mn-**5**	1.25×10^{-3}	1	DB18-C-6	10	15	42%	210
3	Mn-**4**	4.0×10^{-4}	1	–	–	–	18%	90
4	Mn-**4**	4.0×10^{-4}	1	–	–	15	7%	35
5	Mn-**5**	4.0×10^{-4}	10	–	–	–	31%	155
6	Mn-**5**	4.0×10^{-4}	10	–	–	15	31%	155

[a] Reaction conditions: CH_2Cl_2/H_2O $v/v = 1.25/1$; $T = 0°C$; pH 9.5–10.0; 1-dodecene/P = 500. L = *N*-hexylimidazole.
[b] Average values based on three independent experiments.

4. Experimental section

^{1}H-NMR spectra were recorded on Bruker WP80SY or Bruker AC300 spectrometers. UV-VIS spectra were obtained with a Lambda 6 Perkin-Elmer spectrophotometer. MS-FAB$^+$ mass spectra were performed on an Analytical VG 7070 EQ instrument. Melting points were determined with a Büchi 535 apparatus and are uncorrected. GC analyses were performed on a Varian Model 3700 flame ionization instrument (20 × 0.125 in. OV-101-5% on CHP 100–125 mesh column) and on a Hewlett-Packard 5890 gas chromatograph (30 × 0.5 mm RSL-200 polymethylsiloxane).

4.1. Materials

All the commercially available reagents were used as received; solvents for column chromatography were distilled over $CaCl_2$ prior to use. CH_2Cl_2 used in porphyrin syntheses was a 'Baker analyzed' reagent (0.01% of water) stabilized with amylene.

4.2. Synthesis of porphyrins 1–3

5-[2-Chloro-6-[(18-crown-6)methyloxy]-phenyl-10,15,20-tri-(2,6-dichlorophenyl) porphyrin, **1**. A solution of porphyrin **6** [11]a (100 mg, 0.115 mmol) in DMA (70 ml) was stirred for 30 min at 60°C in the presence of Cs_2CO_3 (650 mg, 2 mmol), then the functionalized 18-crown-6 **8** [10]a (220 mg, 0.575 mmol) was added. Stirring went on for further 96 h at 60°C. After this time the solvent was evaporated in vacuo, the residue taken up in CH_2Cl_2 and washed with H_2O. The organic phase was dried ($MgSO_4$), evaporated and the crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 95:5). 60 mg of compound 1 was obtained (44%) as a purple solid. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = -2.50$ (2H, s), 2.05–3.60 (36H, br s), 7.24 (1H, d), 7.42 (1H, d), 7.81 (10H, s), 8.80 (8H, m). UV-Vis (CH_2Cl_2): $\lambda_{max} = 418$ nm; $\epsilon = 190\,000$ dm^3 mol^{-1} cm^{-1}.

5-[2-Chloro-6-[9-(18-crown-6)nonyloxy]phenyl-10,15,20-tri-(2,6-dichlorophenyl)porphyrin, **2**. This compound (48 mg, 45% yield) was synthesized from **6** (73 mg, 0.084 mmol) and crown ether **9** [10]a (198 mg, 0.41 mmol) following the procedure described above. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = -2.50$ (2H, s), 1.52 (16H, m), 2.03–3.60 (25H, br s), 7.25 (1H, d), 7.42 (1H, d), 7.80 (10H, m), 8.82 (8H, m). UV-Vis (CH_2Cl_2): $\lambda_{max} = 418$ nm; $\epsilon = 235\,000$ dm^3 mol^{-1} cm^{-1}.

5-[2,6-Dichloro-3-[9-(18-crown-6)nonyloxy]phenyl-10,15,20-tri-(2,6-dichloro phenyl)porphyrin, **3**. From porphyrin **7** [11]b (160 mg, 0.18 mmol) and crown ether **9** (261 mg, 0.54 mmol) compound **3** (54 mg, 23%) was obtained as described above. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = -2.50$ (2H, s), 1.52 (16H, m), 2.15–3.60 (25H, m), 7.81 (11H, m), 8.80 (8H, m). UV-Vis (CH_2Cl_2): $\lambda_{max} = 418$ nm; $\epsilon = 295\,000$ dm^3 mol^{-1} cm^{-1}.

4.3. Synthesis of porphyrin 4 and precursors 14 and 16

11,12-(3-t-Butyl)benzo-2,3-(3-formyl)benzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene, **15**. Diol **12** (see Scheme 2), synthesized by reaction of 3-*t*-butylcatechol with 2-(2-chloroethoxy)ethanol according to a reported procedure [10]b, was reacted at 0–5°C with methanesulphonyl chloride in pyridine affording **13** in 60% yield after purification by column chromatography (silica gel, AcOEt/petroleum ether 4:1). ^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 1.25$ (9H, s), 3.05 (6H, s), 3.70–4.45 (16H, m), 6.80–6.95 (3H m).

Synthesis of **14** was carried out as follows: a suspension of *t*-BuOK (1.72 g, 15.3 mmol) in dry THF (50 ml) was stirred 30 min at room temperature, then 3,4-dihydroxybenzaldehyde (0.71 g, 5.1 mmol) was added and the temperature raised up to 60°C. One hour later a solution of **13** (2.5 g, 5.1 mmol) in dry THF (150 ml) was dropped into the reaction mixture; after 48 h the reaction was complete and the title prod-

uct was recovered as a white solid (m.p. = 125–126°C) in 40% yield after column chromatography (silica gel, CH_2Cl_2/MeOH 95:5). ^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 1.25$ (9H, s), 3.70–4.32 (16H, m), 6.25–7.05 (4H m), 7.30–7.51 (2H, m), 9.80 (1H, s).

11,12-(3-t-Butyl)benzo-2,3-[3-(6-bromohexyl)methyloxyl]benzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene, **16**. Aldehyde **14** (450 mg, 1 mmol) was reduced with $NaBH_4$ in EtOH/H_2O at room temperature affording the corresponding alcohol **15** (285 mg, 57% yield) after column chromatography (silica gel, $CHCl_3$/EtOH 9/1). This product (0.57 mmol) was dissolved in dry THF under inert atmosphere and treated with 60% NaH (60 mg, 1.5 mmol). After 1h under stirring at room temperature, 1,6-dibromohexane (1.22 g, 5 mmol) was added and the mixture stirred for further 18 h. The solvent was evaporated and the residue was chromatographed (silica gel, $CHCl_3$/EtOH 9/1) affording 240 mg (68%) of **16**. ^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 1.25$ (9H, s), 1.21–2.20 (8H, m), 1.32–2.05 (8H, m), 3.35–3.55 (4H, m), 3.85–4.35 (16H, m), 4.44 (2H,s), 6.63–7.76 (6H, m).

Porphyrin, **4**. Porphyrin **7** (120 mg, 0.13 mmol) was dissolved in 40 ml of dry THF under inert atmosphere then *t*-BuOK (66 mg, 0.58 mmol) was added and the mixture was stirred for 45 min at room temperature. A solution of crown-ether **16** (240 mg, 0.39 mmol) in 15 ml of dry THF was added and stirring went on for further 40 h. The solution was treated with aqueous NH_4Cl and diluted with AcOEt (40 ml). The organic phase was thoroughly washed with water, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (silica gel, $CHCl_3$/EtOH 95:5), followed by crystallization with MeOH, affording 90 mg (48%) of pure **4**. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = -2.50$ (2H, s), 1.25 (9H, s), 1.40–1.84 (4H, m), 2.05 (4H, m), 3.42 (2H, t), 3.80–4.18 (16H, m), 4.30 (2H, t), 4.42 (2H, s), 6.70–6.85 (6H, m), 7.24 (1H, d), 7.60–7.80 (10H, m), 8.55– 8,78 (8H, m). UV-Vis (CH_2Cl_2): $\lambda_{max} = 418$ nm; $\epsilon = 308\,000$ dm^3 mol^{-1} cm^{-1}.

4.4. General procedure for the preparation of Mn(III)-porphyrin complexes

A solution of porphyrin (0.03 mmol) in DMF (30 ml) was stirred under reflux with $Mn(OAc)_2 \cdot 4H_2O$ (735 mg, 3 mmol) for 4 h. After evaporation of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 (150 ml) and washed with water (2 × 30 ml). TLC (silica-gel, $CHCl_3$/EtOH 9:1) showed the complete disappearance of the starting material and UV-Vis spectroscopy the absence of non-metallated porphyrin. Column chromatography (silica-gel, $CHCl_3$/EtOH 9:1) afforded a dark brown powder that was dissolved in CH_2Cl_2 (50 ml) and stirred with a saturated NaCl aqueous solution (50 ml). The organic phase was dried over $MgSO_4$ and the solvent evaporated, affording pure Mn-**1–4** in nearly quantitative yield.

Mn-**1**: MS-FAB$^+$ for$(C_{57}H_{45}Cl_7N_4O_7)Mn^+$, *m/z*: 1224 (cluster, 60%, M + Na$^+$), 1201 (cluster, 100%, M). UV-Vis (CH_2Cl_2): $\lambda_{max} =$ 478 nm; $\epsilon = 87000$ dm^3 mol^{-1} cm^{-1}.

Mn-**2**: MS-FAB$^+$ for$(C_{65}H_{61}Cl_7N_4O_7)Mn^+$, *m/z*: 1336 (cluster,100%, M + Na$^+$). UV-Vis (CH_2Cl_2): $\lambda_{max} = 478$ nm; $\epsilon = 92000$ dm^3 mol^{-1} cm^{-1}.

Mn-**3**: MS-FAB$^+$ for$(C_{65}H_{60}Cl_8N_4O_7)Mn^+$, *m/z*: 1370 (cluster, 100%, M + Na$^+$). UV-Vis (CH_2Cl_2): $\lambda_{max} = 478$ nm; $\epsilon = 101000$ dm^3 mol^{-1} cm^{-1}.

Mn-**4**: MS-FAB$^+$ for$(C_{75}H_{64}Cl_8N_4O_8)Mn^+$, *m/z*: 1510 (cluster, 100%, M + Na$^+$), 1487 (cluster, 20%, M). UV-Vis (CH_2Cl_2): $\lambda_{max} =$ 478 nm; $\epsilon = 99000$ dm^3 mol^{-1} cm^{-1}.

4.5. Alkene epoxidation

Reactions were carried out in a 20 ml flask equipped with a teflon lined screw cap and magnetic stirrer, thermostatted at 0 ± 0.2°C with circulating ethanol by a Haake F3 Cryostat. Stirring was maintained at the maximal rate

achievable (1300 ± 50 rpm) in order to ensure the best contact between the organic and the aqueous phase. The flask was charged with: (i) 1 ml of a 1.0×10^{-3} M solution of Mn(III)-porphyrin (P) in CH_2Cl_2; (ii) 1 ml of a 0.5 M solution of 1-dodecene in CH_2Cl_2 containing decane (0.25 M) as internal standard for gas-chromatography; (iii) 25 μl (L/P = 1) or 250 μl (L/P = 10) of a 4.0×10^{-2} M solution of *N*-hexylimidazole in CH_2Cl_2; (iv) (for reactions carried out with Mn-**5**) 25 μl (CE/P = 1) or 250 μl (CE/P = 10) of a 4.0×10^{-2} M solution of crown-ether in CH_2Cl_2. In each case the final volume was brought to 2.5 ml with CH_2Cl_2. The solution was stirred 5 min then 2.1 ml of NaOCl 0.7 M ($OCl^-/S = 3$) were added to the flask. The pH of NaOCl was previously adjusted to 9.5–10.0 with solid $NaHCO_3$. The mixture was stirred and samples were taken at different times and analysed by G.C.

For reactions run in the presence of KOAc, the organic phase was equilibrated with solid KOAc by stirring for 10 min, then the aqueous NaOCl solution was added.

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